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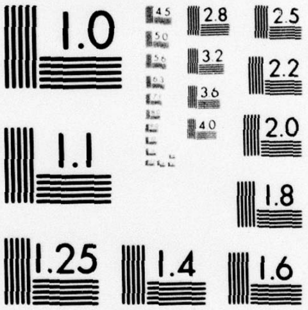

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INTERNATIONAL CONFERENCE ON RADIATION EFFECTS IN SEMICONDUCTORS

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24 January 1977

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Selected papers given at this Conference are briefly reviewed. The meeting emphasized how much is still unknown concerning the nature of defects in semiconductors other than silicon, as well as the need to develop other microscopic probes for investigating materials that are not readily amenable to ESR studies.

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INTERNATIONAL CONFERENCE ON RADIATION EFFECTS IN SEMICONDUCTORS

The 9th International Conference on Radiation Effects in Semiconductors was held in Dubrovnik, Yugoslavia, 6-9 September 1976, under the sponsorship of IUPAP, other international bodies, and the Ruder Bosković Institute, Zagreb, an institute named after an 18th-century Croatian physicist and mathematician who was born in Dubrovnik. The meeting was, to some extent, a satellite meeting of the 13th International Conference on the Physics of Semiconductors, which took place in Rome a week earlier.

Attendance was estimated at about 150, with a fairly good international representation (no attendance list was provided to the participants, but one was posted on the bulletin board on the last day). The US was well represented, starting with the Program and Internation Advisory Committees, both headed by J.W. Corbett (Albany), and carrying through to the invited speakers (one-third of whom came from the US) and to the contributed papers. A sizable contingent from the USSR was led by the ebullient V.S. Vavilov (Lebedev Phys. Inst., Moscow) who, since the Conference language was English, often acted as interpreter from the floor to help some of his less fluent colleagues deal with the discussion questions. Dr. N.B. Urli (Ruder Bosković Inst.) was the Vice-Chairman of the Program Committee and also headed the local organizing committee.

The program featured invited review papers based largely on semiconductor class (Si, Ge, SiC, diamond, III-V, II-VI, Se-Te) with a few based on radiation-induced phenomena (amorphous-crystalline radiation-induced transitions, ionization effects in defect creation and annihilation) and methods (ion implantation). There were no parallel sessions, and there was ample time for discussions, which were quite animated (sometimes extremely so). The Proceedings of the Conference will be published in the Conference Series of the Institute of Physics (London). As yet, the price of the publication and date of its appearance are not known, although the publication should appear reasonably quickly. For this reason only a brief overview of the meeting will be attempted here.

Although the Conference revealed some recent advances in the general area of defects in semiconductors, it was probably most useful in emphasizing how much is not known and still remains to be done. It is clear that among the elemental semiconductors, the knowledge about defects in silicon is the most complete, while by comparison the state of understanding for germanium is still in its infancy. This is mainly due to the microscopic information obtained by successful electron spin resonance (ESR) experiments in silicon and the lack of success of ESR in germanium. The Conference pointed out the need for more microscopic knowledge of defects in semiconductors so that the behavior of materials other than silicon can be well understood. While ESR is very useful, other microscopic probes need to be developed for the exploration of materials which are not so easily studied by this method. It was also quite evident that the best techniques for obtaining information on the electron thermal property of trapping centers are the transient capacitance experiments.

Perhaps one of the most exciting papers was a post-deadline one by J. Schneider *et al.* (Inst. Appl. Solid State Physics, Freiburg, FRG). They presented evidence for the existence of antisite defects in GaP, $CdSiP_2$ and $ZnGeP_2$. For "very pure" GaP, the ESR spectrum gave evidence of an s-orbital central atom with spin 1/2. The investigators gave arguments which led them to identify the defect as P^{4+} on a Ga^{3+} site. This appears to be the first identification of antisite defects, although J. Van Vechten (IBM, Yorktown Heights, NY) has been predicting their existence in large concentrations for many of the compound semiconductors.

The opening invited paper by J.W. Corbett, reviewing defects in Si, struck the theme of "how little we know" right at the outset. Acknowledging that much information on Si is in hand, he nevertheless went on to point out some major gaps in our knowledge. For example: diffusion measurements in Si have been made for less than half of the elements, the self-diffusion mechanism is still controversial, and the diffusion machanisms for the technically dominant impurities, P and B, are still not universally acceptable. Gold is another technically important impurity that can diffuse by various mechanisms. It has also been claimed that its solubility and diffusion coefficient are enhanced by electron or light irradiation; Corbett incidated that his experiments have failed to confirm the effect of light. The shallow donor and acceptor levels introduced by impurities are well established, but the levels in Co-doped and Pt-doped Si are not fully agreed upon. Here again, less than half of the elements have been investigated as impurities in Si. There is a multiplicity of vacancy defects--from single vacancies to pentavacancies--and there is a whole zoo of defects they form by association with interstitial and substitutional impurities. Similarly, there is a bewildering array of self-interstitial and interstitial-impurity defects; and, once again, less than half of the elements have been looked at in this connection. Corbett felt that more information is needed not merely to satisfy our intellectual curiosity but to help make cheaper and better semiconductor devices. He tossed out the idea of possibly developing enough knowledge to formulate "defect-annihilation" centers that could eliminate vacancies or interstitials at will, and he looked forward to the eventual evolution of "defect engineering."

W.J. Choyke's (Westinghouse, Pittsburgh) invited talk on defects in SiC, which followed Corbett's lecture, illustrated how infinitely worse off our knowledge is of defects in this more complex material. Despite the fact that SiC has been of major interest to the nuclear community as a ceramic for fuel encapsulation and other uses, knowledge of radiation-damage effects in this material is primitive compared to what is known about Si. Choyke had time to describe only five of the centers that have been studied by optical and electronic techniques: a divacancy, di-interstitial C, a C-H center (made by proton bombardment followed by a 700°-900°C anneal), a C-C split-interstitial oriented along 100 , and a graphite-like defect that he believes has a planar hexagonal structure. He expressed the hope that one might eventually be able to unite the study of SiC as a semiconductor with study of this material as a ceramic.

In another invited paper, P. Baruch (Ecole Normale Supérieure, Paris, France) gave an analysis of the effect of radiation on diffusion in Si; the effect is not always an enhancement--it may even be a retardation. The effects are complicated. Thus, the depth profile of boron, after annealing of B-implanted Si, is not explainable by classical diffusion. One has to assume that B must exist both substitutionally and interstitially, each having a different mobility, and that the different types are also affected by the presence of interstitial Si. "Two-stream diffusion" takes place, with a "slow" and a "fast" impurity. Baruch pointed out that in most irradiations there is a non-uniform concentration of defects leading to defect flow--a "defect wind" --and the phenomenon resembles the Kirkendall effect in metallurgy. He showed that the action of the defect wind must be modified by complexes formed by the association of impurities with the radiation-induced defect, the latter dragging the impurity along with it. Baruch reminded the audience that the considerations he had presented had applications to reactor damage of metals as well as to ion-implantation in semiconductors.

H.J. Mayer, H. Mehrer and K. Maier (Inst. Theoret. u. Angewand. Phys. and MPI f. Metallforsch., Stuttgart) described a radioactive tracer technique for measuring self-diffusion, which they applied to intrinsic Si. The feature of the method was the *in situ* formation of (radioactive) ^{31}Si and the use of ion-beam sputtering to section the specimen, the sputtered material being gathered on a collecting foil which could be moved like film in a camera-like device, collecting deposited material for only a few minutes and then moving each exposed segment on for counting. The depth of material removed was measured interferometrically.

According to the authors, the results obtained supported the view that self-diffusion in Si occurs by an extended-interstitial mechanism. This interpretation was vigorously disputed by Van Vechten, who claimed that impurity effects could be involved, but A. Seeger (Stuttgart) replied that great care had been taken to avoid impurities, including carbon, in the material investigated by Mayer *et al.*

The discussion on this paper was only a foretaste of the confrontation which broke out the following day after Seeger gave his invited paper, most of which was dedicated to an interpretation of "swirl" defects which can be observed in dislocation-free high-purity Si. Seeger gave electron microscope evidence that these were due to dislocation loops formed by the condensation of self-interstitials rather than of vacancies, as had been previously assumed. Van Vechten, however, espousing the vacancy interpretation, gave an impromptu ten-minute lecture following Seeger's paper on what an electron microscopist "sees." Van Vechten pointed out that the observation that lattice planes expand is not to be taken as evidence of interstitials. According to his calculations for Si, planes do not collapse about vacancies but, to the contrary, they expand about vacancies. It was clear from the animated exchange which ensued that the controversy remains.

A.F.W. Willoughby (Univ. of Southampton) reported on the effects of one dopant on the diffusion of another in Si, e.g., Ga and P in Si. P was found to enhance the tail of the Ga diffusion by 100-fold, whereas As could produce either a small enhancement or a retardation, depending on the conditions of the experiment.

Vavilov and his colleagues, V.S. Konoplev and A.A. Gippins, gave convincing arguments to show that the two luminescent centers produced by electron irradiation of Si (zero-phonon lines at 0.97 eV and 0.49 eV respectively) are due to carbon impurity. They propose a two-carbon-atom 111 split-interstitial model for the 0.97-eV center and a similar configuration with a nearby oxygen atom as the 0.49-eV center.

L.C. Kimmerling (Bell Telephone Labs, Murray Hill) gave results of the capacitance transient spectroscopy technique to study defect states in electron-irradiated silicon. His experiments on silicon irradiated at 10 K and at room temperature have yielded information on energy levels and capture crosssections. He correlated some of the defect states with centers which have been identified by ESR and which exhibit similar production and annealing characteristics. The transient capacitance technique has been used effectively to probe the thermal stability of defects by observing the annealing of some defects and the growth of others as a function of temperature.

J.C. Corelli *et al.* (Rensselaer Polytech. Inst., Troy) reported on optical absorption experiments in very heavily neutron-irradiated silicon (up to 10^{19} n/cm^2). The studies were carried out with polarized light in the region from 709 cm^{-1} to 1317 cm^{-1} with careful alignment of the electric-field vector either normal or parallel to an applied stress.

The data were interpreted as evidence for transitions of shallow donors in disordered silicon containing multiple vacancies and/or interstitials.

D. M. Maher, R. L. Meek and W. M. Gibson (Bell Telephone Labs, Murray Hill) have performed low-temperature irradiations with helium ions on silicon containing stacking faults. Electron microscopy reveals that defect clusters are formed in planar arrays parallel to stacking fault planes. Following annealing, dislocation loop images appear which the authors interpret as being interstitial in nature. In response to a question from the floor, it was admitted that there is no way of knowing whether the defects are vacancies or interstitals, but that they are extrinsic in character and are interpreted as interstitials.

One of the best invited papers was a review of the III-V semiconductors by lAvid Lang (Bell Telephone Laboratories). He pointed out that one of the problems people have in understanding radiation effects in III-V compounds is that workers in the field are used to thinking in terms of Ge and Si. Lang stated that lattice relaxation mechanisms are very important in the III-V compounds and that the behavior of GaAs and GaP is more akin to that of ZnSe and ZnS than to that of Ge and Si. While the focus of the presentation was on GaAs, he covered investigations which have application to the other materials. A large part of his talk involved the deep-level transient spectroscopy (DLTS) results obtained at Bell Labs pointing out that it has been recently demonstrated that injection annealing is due to recombination-enhanced motion rather than charge-state effects. He mentioned the work of Weeks, Tully and Kimmerling which showed that multiphonon emission is the mechanism for radiation-enhanced motion, a phenomenon which resembles the Pooley-Hersh mechanism for defect production by irradiation in the alkali halides. Lang stated that there are some unanswered questions concerning defect intorduction in GaAs. Carrier removal and photoluminescence data do not agree, and no experiment has been performed to study electron damage vs. particle energy systematically. In addition, there is a need for a sensitive technique which can be used to probe the III-V compounds on a microscopic level. ESR is very difficult in the III-V compared with Si, for which it has been so successful.

Some evidence was presented by T.V. Mashovets (Ioffe Institute, Leningrad) that radiation-induced defects interact with impurities in InSb. Because the interaction between impurities and Frenkel pair components takes place at liquid helium temperatures, it was concluded that at least one of the Frenkel pair components is mobile in InSb at temperatures as low as 4.2 K.

There seems to be considerable interest in InP, with evidence given for introduction of deep levels which are stable at room temperatures. N.P. and G.P. Kekelidze (Tbilisi State University) have found that fast neutrons produced deeper levels than those produce by fast electrons.

Van Vechten presented a theoretical discussion of threshold energies for Frenkel pair production in semiconductors. He fearlessly stated that the minimum transfer energy for cation pair production is less than for anion pair production in the tetrahedral IV-IV, III-V and II-VI semiconductors. If he is right, this means that several of the experimentally determined displacement-threshold energies have incorrect designations. Needless to say, there is some controversy over these conclusions.

A paper by S.T. Pantelides (IBM, Yorktown) and J. Bernholc (Univ. of Lund) was very interesting in that the details of the band structure of silicon were used to calculate the band density of states. The resulting density of states was then used successfully to calculate photoionization cross sections for a number of shallow and deep acceptors in silicon.

Dennis and Hale have used ESR as a probe of the amorphization process in ion-implanted silicon. By measuring the critical dose required for the transformation from crystalline to amorphous silicon, they were able to revise the transformation model of F. Morehead and B. Crowder (*Rad. Effects* 6 27 (1970)) to account for the total energy lost in atomic processes. The experiments were in good agreement with the model for low mass ions and at low temperatures. As the temperature inreases, the energy density required for transformation increases. This led the authors to speculate that the migration energy of vacancies may be very important at higher temperatures.

A paper by R. Yagi *et al*. (Int. Phys. & Chem. Research, Wako-Shi and Science Univ. of Tokyo) gave the results of channeling experiments on rutile. They identified interstitial Ti ions and confirmed an earlier ESR identification by comparing ESR data with the channeling data.

G. Watkins (Lehigh U., Bethleham, Pa.) undertook the difficult assigment of reviewing defects in the II-VI compounds--a major chore which he accomplished with great lucidity. G. Landwehr (Univ. of Würzburg) very thoroughly reviewed what is known about defects in Te, which has suffered from having few applications to stimulate industrial interest.

The next Conference in this series is scheduled to be held in 1978 at Cannes, on the French Riviera.